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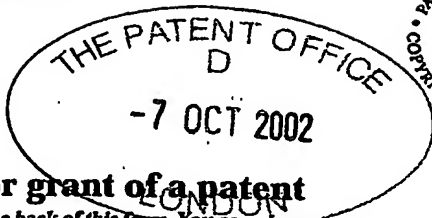
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9872

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07 OCT 2002

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UNITED KINGDOM

Patents ADP number (If you know it)

If the applicant is a corporate body, give the country/state of its incorporation

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4. Title of the invention

PROCESS

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BROOKE, Caron

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PROCESS

The present invention relates to a process for the production of alkenyl carboxylates, and, in particular to a process for the production of vinyl acetate.

Vinyl acetate is generally prepared commercially by contacting ethylene and acetic acid with molecular oxygen in the presence of a catalyst active for the production
5 of vinyl acetate. The process may be carried out in either a fixed bed or a fluid bed reactor. A process employing a fixed catalyst bed is described, for example, in EP-A-0845453. Processes employing a fluidised catalyst bed are described, for example, in EP-A-0672453, EP-A-0685449, EP-A-0685451, EP-A-0985655 and EP-A-1008385.

Catalysts active for the production of vinyl acetate may typically comprise a
10 Group VIII metal, such as palladium; a co-promoter, such as gold, copper, cerium or mixtures thereof; and, optionally, a co-promoter, such as potassium acetate. For example, catalysts active for the production of vinyl acetate are described in GB 1 559 540; US 5,185,308 and EP-A-0672453 the contents of which are hereby incorporated by reference. EP-A-0672453, for example, describes palladium containing catalysts and
15 their preparation for fluid bed vinyl acetate processes.

A commercial vinyl acetate process is generally operated as a continuous process. During the start-up and operation of the process, process upsets may arise. In addition to unexpected process upsets, a commercial process is generally subject to planned shut-downs, for example, for the periodic maintenance of the plant and/or
20 replacement of deactivated catalyst with fresh catalyst.

Where a process upset occurs in, for example, the production of vinyl acetate from ethylene, acetic acid and oxygen, the oxygen feed to the reaction zone is usually

shut-off. In addition it may or may not also be desirable to shut off the acetic acid feed to the reaction zone. Whether or not the acetic acid feed is shut-off, the catalyst will be exposed to ethylene in the substantial absence of oxygen. In general, a similar procedure will be followed for a planned shut-down, in that the oxygen feed to the reaction zone is generally shut-off prior to shutting-off the acetic acid feed. The catalyst will then be left exposed to ethylene in the substantial absence of oxygen.

It has been found that where catalysts suitable for use in the production of alkenyl carboxylates, such as vinyl acetate, are exposed to significant levels of olefin in the absence of oxygen or at low concentrations of oxygen, such as during process start-up or shut-downs, the catalyst shows unexpectedly low activity on starting-up or restarting the process. Due to this unexpected loss in catalytic activity (catalyst inhibition), the production rate is low and significantly lower than expected.

Furthermore, as a result of this reduction in catalytic activity, oxygen may not be consumed thereby creating an accumulation of unreacted oxygen in the reactor and increasing the risk of explosion.

Thus, there remains a need for an improved process for the production of alkenyl carboxylates, such as vinyl acetate. In particular, there is a need for a process in which catalytic activity is not reduced on contact with olefin or olefin and carboxylic acid in the substantial absence of oxygen.

Thus, according to the present invention there is provided a process for the production of an alkenyl carboxylate by contacting in a reaction zone at elevated temperature, at least one alkene and at least one carboxylic acid with a molecular oxygen-containing gas, in the presence of a catalyst comprising a Group VIII metal, a catalyst promoter and an optional co-promoter, wherein in said process, and prior to contacting the catalyst with the molecular oxygen-containing gas, the catalyst is contacted, in the substantial absence of oxygen, with the alkene or the alkene and the carboxylic acid, such that the period of contact of the catalyst with the alkene or the alkene and the carboxylic acid, is insufficient to inhibit catalytic activity.

In an embodiment of the process of the present invention, the alkenyl carboxylate is vinyl acetate. Thus, the present invention accordingly provides a process for the production of vinyl acetate by contacting in a reaction zone at elevated temperature, ethylene and acetic acid with a molecular oxygen-containing gas, in the

presence of a catalyst comprising a Group VIII metal, a catalyst promoter and an optional co-promoter, wherein in said process, and prior to contacting the catalyst with the molecular oxygen-containing gas, the catalyst is contacted, in the substantial absence of oxygen, with ethylene or ethylene and acetic acid, such that the period of contact of the catalyst with ethylene or ethylene and acetic acid, is insufficient to inhibit catalytic activity.

Typically, the production of alkenyl carboxylate such as vinyl acetate is carried out heterogeneously with the reactants being present in the gas phase or as a mixture of gas and liquid phases.

The alkene may be any suitable alkene or a mixture of alkenes, but is preferably a C₂-C₄ alkene, such as ethylene.

The alkene may be fed in substantially pure form or admixed with other materials, such as, for example, other alkenes or hydrocarbons, hydrogen or inert materials. For example, where the alkene is ethylene, the ethylene may be fed in substantially pure form or may be fed admixed with one or more of nitrogen, methane, ethane, carbon dioxide and water in the form of steam or one or more of hydrogen, C₃/C₄ alkenes or alkanes.

The alkene may comprise fresh and/or recycle alkene.

The fresh and recycle alkene, for example, ethylene, may be introduced into the reaction zone either as separate feed streams or as a single feed stream comprising both fresh and recycle alkene.

The carboxylic acid may be any carboxylic acid or a mixture of carboxylic acids, but is preferably a C₂-C₄ carboxylic acid, such as acetic acid.

The alkenyl carboxylates that may be produced in the process of the present invention include vinyl propionate, allyl acetate or allyl propionate.

Preferably, however, where the alkene is ethylene, the carboxylic acid used in the process of the present invention is acetic acid, such that the alkenyl carboxylate produced is vinyl acetate.

The carboxylic acid may be introduced into the reaction zone in liquid form or in vapour form. Where the process is a fixed bed process then the carboxylic acid is preferably introduced in to the reaction zone in vapour form. Where the process is a fluid bed process then the carboxylic acid is preferably introduced in to the reaction

zone as a liquid spray.

The carboxylic acid may comprise fresh and/or recycle acid.

The fresh and recycle carboxylic acid may be introduced into the reaction zone either as separate feed streams or as a single feed stream comprising both fresh and
5 recycle acid.

The carboxylic acid may comprise at least a portion of the acid obtained from downstream processes such as from the separation of the acid from a mixture of the acid/alkenyl carboxylate/water.

The molecular oxygen-containing gas may be any suitable molecular oxygen-
10 containing gas and may suitably be air or a gas richer or poorer in molecular oxygen than air. A suitable molecular oxygen-containing gas may be, for example, oxygen diluted with a suitable diluent, for example nitrogen, argon or carbon dioxide. Preferably, the oxygen-containing gas is essentially pure oxygen.

Under normal reaction conditions the alkene, carboxylic acid and oxygen
15 reactants may be introduced into the reaction zone in any suitable proportions for the production of the alkenyl carboxylate. For example, the alkene may be present in the feed to the reaction zone in a range between 30 and 85mol% of the total reaction composition, preferably at least 50mol%, such as in an amount of at least 60mol% of the total reaction composition. The carboxylic acid may be present in the feed to the
20 reaction zone in a range between 2 and 30mol% of the total reaction composition, preferably 5 to 15mol%. The molecular oxygen present in the feed to the reaction zone is controlled by flammability constraints. In a fixed bed reactor the molecular oxygen is preferably introduced to the reactor via the recycle gas and the feed to the reaction zone must be such that the mixture is non-flammable, for example the molecular oxygen may
25 be present in a range 2 to 9mol% of the total reaction composition. In a fluid bed reactor the oxygen-containing gas is preferably added directly to the reactor and the molecular oxygen may be present at a higher level, for example, in a range 1 to 15 mol% of the total reaction composition. A balance of an inert gas, preferably one or more of nitrogen, carbon dioxide and argon may also be present in the reactant feed.

30 The catalyst for use in the process of the present invention is any promoted Group VIII metal suitable for the production of an alkenyl carboxylate from an alkene, carboxylic acid and a molecular oxygen-containing gas.

Where vinyl acetate is the alkenyl carboxylate, the catalyst suitable for use in the production of vinyl acetate in a fixed bed process may comprise any suitable catalyst known in the art, for example, as described in GB 1 559 540 and US 5,185,308.

GB 1 559 540 describes a catalyst active for the preparation of vinyl acetate by the reaction of ethylene, acetic acid and oxygen, the catalyst consisting essentially of:

(1) a catalyst support having a particle diameter of from 3 to 7 mm and a pore volume of from 0.2 to 1.5 ml/g, a 10% by weight water suspension of the catalyst support having a pH from 3.0 to 9.0,

(2) a palladium-gold alloy distributed in a surface layer of the catalyst support, the surface layer extending less than 0.5 mm from the surface of the support, the palladium in the alloy being present in an amount of from 1.5 to 5.0 grams per litre of catalyst, and the gold being present in an amount of from 0.5 to 2.25 grams per litre of catalyst, and

(3) from 5 to 60 grams per litre of catalyst of alkali metal acetate.

US 5,185,308 describes a shell impregnated catalyst active for the production of vinyl acetate from ethylene, acetic acid and an oxygen containing gas, the catalyst consisting essentially of:

(1) a catalyst support having a particle diameter from about 3 to about 7 mm and a pore volume of 0.2 to 1.5 ml per gram,

(2) palladium and gold distributed in the outermost 1.0 mm thick layer of the catalyst support particles, and

(3) from about 3.5 to about 9.5% by weight of potassium acetate wherein the gold to palladium weight ratio in said catalyst is in the range 0.6 to 1.25.

A catalyst suitable for use in the production of vinyl acetate in a fluid bed process may comprise a Group VIII metal, a catalyst promoter and an optional co-promoter.

With regards to the Group VIII metal, the preferred metal is palladium. Suitable sources of palladium include palladium (II) chloride, sodium or potassium tetrachloropalladate, (II), (Na_2PdCl_4 or K_2PdCl_4), palladium acetate, palladium (II) nitrate or palladium (II) sulphate. The metal may be present in a concentration of greater than 0.2% by weight, preferably greater than 0.5% by weight based upon total weight of catalyst. The metal concentration may be as high as 10% by weight.

Generally, the higher the active metal loading in a catalyst suitable for use in vinyl acetate production, the more catalytically active it will be.

In addition to the Group VIII metal, the catalyst for the production of vinyl acetate comprises a promoter. Suitable promoters include gold, copper, cerium or mixtures thereof. A preferred promoter is gold. Suitable sources of gold include gold chloride, tetrachloroauric acid (HAuCl_4), NaAuCl_4 , KAuCl_4 , dimethyl gold acetate, barium acetoaurate or gold acetate. The preferred gold compound is HAuCl_4 . The promoter metal may be present in an amount of from 0.1 to 10% by weight in the finished catalyst.

The catalyst suitable for use in the production of vinyl acetate may also comprise a co-promoter material. Suitable co-promoters include Group I, Group II, lanthanide or transition metals, for example cadmium, barium, potassium, sodium, manganese, antimony, and/or lanthanum, which are present in the finished catalyst as salts, e.g. an acetate salt. The preferred salts are potassium or sodium acetate. The co-promoter is preferably present in the catalyst composition in a concentration of 0.1 to 15% by weight of catalyst, more preferably, from 1 to 5% by weight.

Where a liquid acetic acid feed is used the preferred concentration of co-promoter salt is up to 6% by weight, especially 2.5 to 5.5%. Where the acid is introduced in the vapour phase the co-promoter salt is preferably present in a concentration up to 11 wt%.

The catalyst may be a supported catalyst. Suitable catalyst supports include porous silica, alumina, silica/alumina, titania, silica/titania or zirconia. Where the catalyst is a catalyst suitable for use in the production of vinyl acetate, and in particular for use in a fluid bed process, the support is preferably silica, and, suitably, the support may have a pore volume from 0.2 to 3.5 ml per gram of support, a surface area of 5 to 800 m^2 per gram of support and an apparent bulk density of 0.3 to 1.5 g/ml.

In a fluid bed reactor the particles of the catalyst are maintained in a fluidised state by a suitable gas flow through the system. Excess flow rate may cause channeling of the gas through the reactor which decreases conversion efficiency.

A typical catalyst useful in the production of vinyl acetate in a fluidised bed reaction may have the following particle size distribution:-

0 to 20 microns

0-30 wt%

20 to 44 microns	0-60 wt%
44 to 88 microns	10-80 wt%
88 to 106 microns	0-80 wt%
>106 microns	0-40 wt%
>300 microns	0-5 wt%

Persons skilled in the art will recognize that support particles sizes of 44, 88, 106 and 300 microns are arbitrary measures in that they are based on standard sieve sizes. Particle sizes and particle size distributions may be measured by an automated laser device such as a Microtrac X100.

The catalyst may be prepared by any suitable method. For example the catalyst for the production of vinyl acetate may be prepared by the method detailed in EP-A-0672453, the contents of which are hereby incorporated by reference.

The method of catalyst preparation may be varied to optimise catalyst performance based on maximising yield and selectivity.

In the process of the present invention, the catalyst is contacted, prior to contact with the molecular oxygen-containing gas, with either alkene alone or alkene together with the carboxylic acid in the substantial absence of oxygen. The period of contact of the alkene or the alkene and carboxylic acid should be such that catalytic activity is not reduced, that is, that the catalyst does not become inhibited. A catalyst becomes inhibited if it shows more than 10% lower activity than that expected under those conditions. Thus, a fresh catalyst will be inhibited if it shows an activity more than 10 % lower than the initial activity expected from a fresh catalyst. Catalyst which has been employed in the process prior to a shut-down will have become inhibited if it shows more than a 10% loss in activity on restarting the process compared to its activity immediately prior to shut-down.

The period of contact before the catalyst becomes inhibited may vary depending on numerous factors, such as the specific nature of the catalyst employed, the sensitivity of the catalyst to the alkene and carboxylic acid, the nature of the reactant(s) to which the catalyst is exposed and their partial pressures, and also temperature. Typically, however, in the production of vinyl acetate using a promoted Group VIII metal, such as palladium, the period of contact of the catalyst with ethylene or ethylene and acetic acid, in the substantial absence of oxygen, is preferably in the range [>0 to 18] hours, more

preferably, in the range, [>0 to 12] hours and especially, in the range [>0 to 6] hours.

Catalyst inhibition may be more severe in the presence of combinations of reactant feeds in the substantial absence of oxygen. Thus, where the catalyst is contacted with alkene and carboxylic acid, such as ethylene and acetic acid, in the substantial absence of oxygen, the period of contact, is preferably less than the period of contact period with alkene alone. Suitably, therefore, the contact period is in the range [>0 to 12] hours, preferably, in the range [>0 to 6] hours.

Where the period of contact is likely to cause inhibition of the catalyst, for example, if, in the absence of other action, it is likely to exceed the ranges described above, then it may become necessary to mitigate or prevent the inhibition. This may be done, for example, by reducing the partial pressure of either the alkene and/or the carboxylic acid from the reaction zone, preferably by removing both from the reaction zone, for example by purging the reaction zone with an inert gas. Alternatively, or additionally, it may be desirable to change other factors that may affect the period of contact before the catalyst becomes inhibited, such as by reducing the temperature.

By minimizing the contact time of the catalyst with the alkene or alkene and carboxylic acid, in accordance with the present invention, reduction in catalytic activity can be avoided or at least mitigated thereby avoiding prolonged start-up periods and/or reducing the time taken before the process recovers full production rates after a shutdown,

Fluid bed processes may be run at higher nominal molecular oxygen levels in the reaction zone than in fixed bed processes. Thus, for example, on start-up of a fluid bed process, in which the catalyst is, prior to the introduction of the molecular oxygen-containing gas, contacted with alkene or alkene and carboxylic acid for a prolonged period of time, the catalyst loses activity and therefore the oxygen introduced into the reaction zone is unconsumed, leading to high levels of oxygen in the reaction zone outlet and an increased risk of explosion. By employing the process of the present invention unsafe operation is mitigated.

The activity of a catalyst may be determined by any suitable method known in the art, for example, by analysis of samples of catalyst withdrawn from the catalyst bed. Typically, in a fluid bed process for the manufacture of vinyl acetate, the production rate of vinyl acetate is suitably determined by calculating the amount of vinyl acetate

product produced per unit catalyst per unit time. For example, the space-time yield may be measured as the production of vinyl acetate in grammes of vinyl acetate produced per kilogram of catalyst per hour (gVA/kg-cat/hr).

5 The process of the present invention may be carried out as a fixed bed or a fluid bed process, preferably, a fluid bed process.

- The process of the present invention may be carried out at a temperature from 100 to 400°C and at atmospheric or at greater than atmospheric pressure, for example, at up to 20 barg.

10 For example, the process for the production of vinyl acetate when carried out in a fluid bed reaction zone may suitably be operated at a temperature from 100 to 400°C, preferably 140 to 210°C and a pressure of 1×10^5 to 2×10^6 Pa gauge (1 to 20 barg), preferably 6×10^5 to 1.5×10^6 Pa gauge (6 to 15 barg), especially 7×10^5 to 1.2×10^6 Pa gauge (7 to 12 barg).

15 The process for the production of vinyl acetate when carried out in a fixed bed reaction zone may suitably be operated at a temperature from 100 to 400°C, preferably 140 to 180°C and a pressure of 1×10^5 to 2×10^6 Pa gauge (1 to 20 barg), preferably 6×10^5 to 1.5×10^6 Pa gauge (6 to 15 barg), especially 7×10^5 to 1.2×10^6 Pa gauge (7 to 12 barg).

20 The invention will now be illustrated by reference to the following Examples and Figures.

Figure 1 is a graph illustrating the effect on catalytic activity of pre-treating a vinyl acetate catalyst with ethylene or a mixture of ethylene and acetic acid, prior to contacting with oxygen.

25 Figure 2 is a graph illustrating the effect on catalytic activity of pre-treating a vinyl acetate catalyst with a mixture of ethylene and acetic acid, prior to contacting with oxygen.

Figure 3 is a graph illustrating the effect on vinyl acetate fluidized bed reactor outlet oxygen levels by pre-treating the catalyst with ethylene or a mixture of ethylene and acetic acid.

30 Examples

Example 1

These experiments demonstrate the effect on catalytic activity of

- 1) contacting a vinyl acetate catalyst with ethylene prior to contacting with oxygen
- 2) contacting a vinyl acetate catalyst with a mixture of ethylene and acetic acid prior to contacting with oxygen.

5 A 1.8g sample of a promoted palladium vinyl acetate catalyst was mixed with 20-22g of inert diluent, and contacted for a period of 18, 66 or 138 hours with either ethylene or a mixture of ethylene and acetic acid, at 160°C and 8 barg in a fluidised bed microreactor.

10 The flow rates of ethylene and acetic acid were 0.49 mol/hr and 0.05 mol/hr respectively. The fluidised bed microreactor had a diameter of 1" and was fitted with baffle trays. Gas flow was provided through a plenum at the base of the unit, and also from a small sparger mounted within the fluid bed.

15 After the pre-treatment with ethylene or a mixture of ethylene and acetic acid, each catalyst was tested in the fluidised bed microreactor operated at 160°C and 8 bar. A reaction mixture of 52mol% ethylene, 5mol% acetic acid and 1.9mol% oxygen, with a nitrogen balance at a total flow rate of 0.93 mol/hr was fed into the reactor. Samples were removed periodically and vinyl acetate was measured by GC.

20 The results are shown in Figs. 1 and 2. Figure 1 shows the activity profile (space time yield (STY) in gVA/Kg-cat/hr) for a fresh, non pre-treated catalyst (catalyst 1) compared to equivalent catalysts (2 and 3) that have been pre-treated by exposure to ethylene and a mixture of ethylene and acetic acid respectively for 138 hours. It can be seen that both catalysts 2 and 3 have a significantly reduced initial activity compared to the non-pretreated catalyst. With time on stream the catalysts start to regain some of the lost activity.

25 It is also clear that the catalyst exposed to a mixture of ethylene and acetic acid (catalyst 3) is more severely inhibited than that exposed to ethylene alone (catalyst 2).

Figure 2 shows a comparison of the non pre-treated catalyst (catalyst 1, as above) with catalysts that have been pre-treated in a mixture of ethylene and acetic acid for two different periods of time, namely 18 hours (catalyst 4) and 138 hours (catalyst 3, as above) respectively.

30 It can be seen that the initial extent of catalyst inhibition is related to the length of time for which the catalyst was exposed to the mixture of ethylene and acetic acid.

Example 2

300 g samples of promoted palladium vinyl acetate catalysts were pre-treated for 18 hours (unless otherwise stated) in a fluidised bed reactor with a diameter of 1½”(38mm), fitted with baffle trays with the materials as specified in Table 1. Gas flow was provided through a plenum at the base of the unit, and also from a small sparger mounted within the fluid bed. Heating was provided by a three-zone oil jacket, and the feed gases were pre-heated before entering the reactor. The reactor was operated at 8 barg and 155°C. Nitrogen was used in all pre-treatments unless otherwise stated.

Catalyst	Pre-treatment atmosphere
5	Ethylene, acetic acid, vinyl acetate, nitrogen
6	Ethylene, nitrogen (with purge*)
7	Ethylene, acetic acid, nitrogen
8	Acetic acid, nitrogen
9	Ethylene, nitrogen

*catalyst purged overnight with nitrogen after ethylene/nitrogen pre-treatment but before reaction.

After the pre-treatment the reactor was purged with nitrogen for 1 hour. A feed comprising 60 mol% ethylene, 12 mol% acetic acid, 6.8 mol% oxygen, balance nitrogen was then fed into the reactor. The reaction was monitored by tracking the oxygen levels into and out of the reactor. The oxygen flow in was recorded in grammes per hour (g/hr) using a mass flow controller. The oxygen levels leaving the reactor were measured using a Servomex oxygen analyser, which reported in weight percent (wt%).

The results are shown in Fig. 3. Figure 3 shows the reactor outlet oxygen levels for pre-treated catalysts 5 to 9 compared to the inlet oxygen level. Varying levels of inhibition can be observed based on the time taken for the oxygen outlet to move away from the slope for the oxygen feed level, denoting oxygen conversion.

As can be seen from Fig. 3, catalyst 7, pre-treated with ethylene, acetic acid and nitrogen was the most inhibited, and was more inhibited than a catalyst pre-treated with ethylene and nitrogen alone (catalysts 6 and 9). The nitrogen purge used on catalyst 6 before start-up appeared to make little difference.

Although the presence of acetic acid and ethylene gives more inhibition than ethylene alone, the catalyst pre-treated with acetic acid and nitrogen only (catalyst 8)

showed little or no inhibition compared to a fresh catalyst. This therefore indicates that an atmosphere comprising ethylene is required for inhibition in this system.

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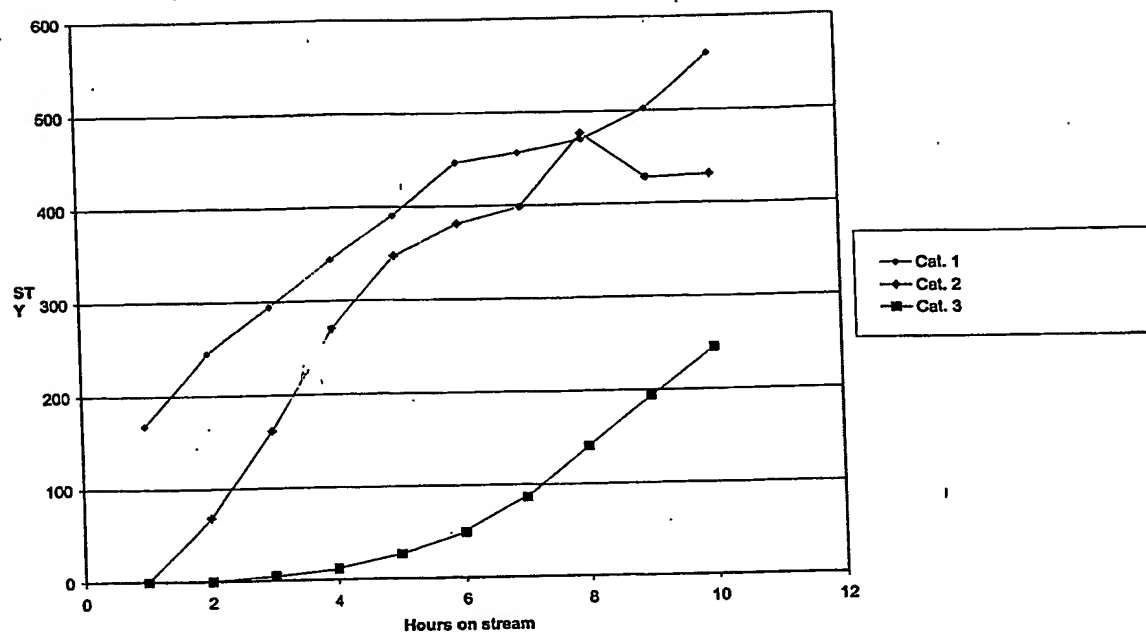


Figure 1

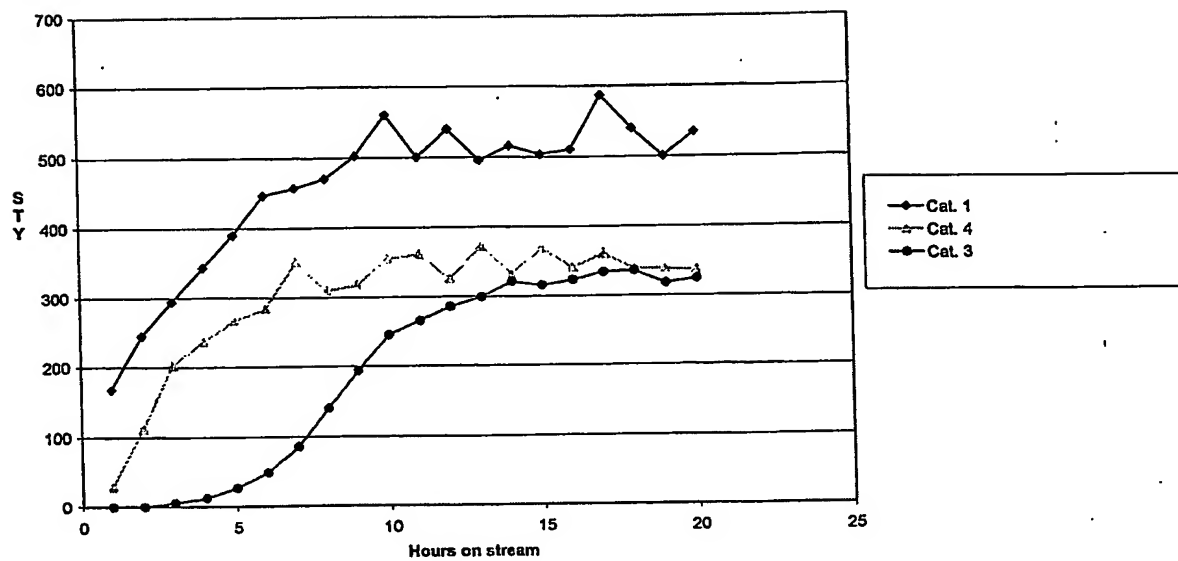


Figure 2

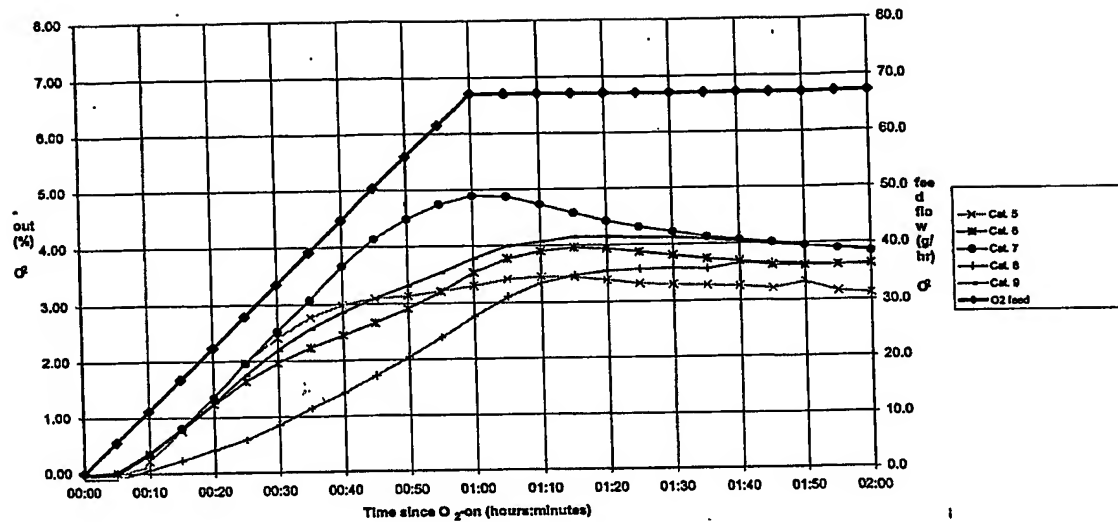


Figure 3:

PCT Application

GB0304220



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